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Procedia Engineering 42 (2012) 1711 – 1719

**Procedia
Engineering**www.elsevier.com/locate/procedia

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Sonocatalytic oxidative desulfurization of thiophene and its derivatives

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Abstract

Currently, the sulfur level in diesels is limited to 10 and 15 ppm in Europe and USA respectively, since the organosulfur compounds available in fuels emit corrosive SO₂ gases into atmosphere during combustion, thus leading to acid rain. A lot of processes such as hydrodesulfurization (HDS), oxidative desulfurization (ODS) etc. have been used to reduce sulfur level in fuels and ODS, which is alternative to conventional HDS, is much more efficient in removing benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives as compared with HDS and more economical. One of very powerful oxidation systems used in ODS is H₂O₂-formic acid and removal of alkyl-substituted derivatives of T, BT and DBT with this oxidation system is easier than that with H₂O₂-phosphotungstic acid catalyst system due to the steric hindrance of alkyl groups adjacent to sulfur atom because phosphotungstic acid is a bulky catalyst. In this work, oxidative desulfurization reactions of the model compounds, thiophene (T), 2-methylthiophene (2-MT) and 2,5-dimethylthiophene (2,5-DMT), which have the lowest reactivity in ODS, on sonication at low H₂O₂ (O) / F (formic acid) / S (organosulfur solution) volume ratios were carried out sequentially in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst at 30 and 40 °C. First, the solution of the relevant model sulfur compound in n-heptane was put into a steel batch reactor and later, reactions were performed by adding mixture of 35 % H₂O₂, formic acid and TBAB onto the organic phase. After each reaction cycle, the aqueous phase was removed by a separation funnel and the oxidative desulfurization reaction of the remaining treated organic phase was repeated three or four times with reuse of the same amounts of fresh hydrogen peroxide, formic acid and TBAB as in the first reactions at 30 and 40 °C for 15 min. After every reaction cycle, the sulfur compounds in heptane were analyzed by using GC with Sulfur Chemiluminescence Detector. Afterwards, the oxidative desulfurization reactions of the model sulfur compounds in heptane were performed for only one cycle in sonoreactor with total amount of oxidation reagents H₂O₂, formic acid and the same amount of TBAB used in the former multi-cycle reactions at 30 and 40 °C for 15 and 60 min. It was observed that the total conversions of model sulfur compounds obtained from multicycle reactions were higher than its conversions obtained from single-cycle

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reactions with total amount of oxidation reagents used in the multicycle reaction. The same method was also applied to diesel fuel sample and it was shown that high sulfur removal is reached.

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Keywords: Sonication; thiophene; sonoreactor

1. Introduction

Desulfurization of fuels has gained a considerable importance recently and the maximum amount of sulfur in diesel fuels with the new regulations has been determined as 10 ppm, 15 ppm in Europe and USA since 2006, respectively [1]. The reason of the restrictions is the hazardous effects imposed on the environment by the sulfur in fuels. As a result of combustion of organosulfur compounds, released SO₂ leads to acid rain, corrodes internal parts of engines in addition to poisoning catalytic converters in them [2-4].

The main organic sulfur compounds in petroleum fractions are thiols, sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes, naphthothiophenes, benzonaphthothiophenes, phenanthro[4,5-b,c,d]thiophenes and their alkyl derivatives [5]. Currently, the most widely used method for reducing sulfur in fuels is HDS (Hydrodesulfurization) in which sulfur are removed in the form of H₂S, but it is not enough to desulfurize sterically hindered aromatic sulfur compounds such as 4,6-DMDBT (4,6-dimethyl dibenzothiophene) adsorption of which on active site of catalyst is prevented due to alkyl groups adjacent to sulfur atom [6].

Aside from HDS, oxidative [7], adsorptive [8], biologic [9] and microwave [10] desulfurization methods have been used. The most promising among the processes is ODS. During ODS, organosulfur compounds are converted to their sulfones, followed by extraction of the sulfones with a polar solvent or adsorption [11]. There are many advantages of ODS, e.g., disuse of expensive catalysts and hydrogen, low reaction temperature and ambient pressure, compared to HDS [12]. Much more important feature is that refractory aromatic sulfur compounds such as BT, DBT and their alkyl-substituted derivatives are more reactive in ODS while they are less reactive in HDS [1,13,14]. The most commonly used oxidant in ODS is hydrogen peroxide [1] and environment friendly since it decomposes to water and oxygen upon heating [15]. To emulsify aqueous and organic phases, two phase transfer catalysts (PTC) used are frequently TBAB and tetraoctylammonium bromide (TOAB) that are quaternary ammonium salts [3]. Also transition metal catalysts [16-18] and catalysts such as acetic acid [19,20], formic acid [7,18,21,22] which increase its oxidizing power by activating H₂O₂ are added to aqueous media. It is found that ODS reactivity increases with electron density on sulfur atom and it is in the order 4,6-DMDBT>4-DMDBT>DBT>R-BT>BT>R-T>T in H₂O₂-formic acid catalyst system [23]. However, if a transition metal catalyst, e.g., phosphotungstic acid instead of formic acid is used, it forms bulky polyoxoperoxo complex with H₂O₂, making more difficult ODS of alkyl-substituted aromatic sulfur compounds due to the steric hindrance of alkyl groups adjacent to sulfur atom and as a result of that, desulfurization yield is lower [24,25].

To further improve the efficiency of ODS, ultrasound studies were also performed [3,26-29]. Ultrasound not only emulsifies aqueous and organic phase in the liquid, but also causes acoustic

cavitation. As the bubbles formed are imploding, they generate locally very high temperatures and pressures [30] and for this reason, reactions are faster in the presence of PTC on sonication [31].

Although there are ample reports concerning thiophene, which has the lowest reactivity in ODS, in the literature, all the reactions were carried out in one cycle, but multiple cycles [19,32-34].

Our object in this study is to search optimum and efficient amounts of H_2O_2 , formic acid and thiophene solution economically on ODS and to remove thiophene and its derivatives completely by conducting the multi-cycle reactions with the same amounts.

2. Experimental Sections

2.1. Materials

Hydrogen peroxide solution (H_2O_2 35%, Riedel De Haen), tetra-n-butylammonium bromide ($\text{C}_{16}\text{H}_{36}\text{BrN} \geq 98\%$, Sigma-Aldrich), tetra-n-octylammonium bromide (TOAB) ($\text{C}_{32}\text{H}_{68}\text{BrN}$, m.p. 95-98 °C, Merck), n-heptane ($\text{C}_7\text{H}_{16} \geq 99\%$, Merck), formic acid (CH_2O_2 98-100 %, Sigma-Aldrich), thiophene ($\text{C}_4\text{H}_4\text{S}$, b.p. 84 °C, Aldrich), 2-methylthiophene ($\text{C}_5\text{H}_6\text{S}$ purum, Aldrich), 2,5-dimethylthiophene ($\text{C}_6\text{H}_8\text{S}$ 98.5 %, Aldrich) as model compounds and T922 diesel oil (0.8406 g/cm^3 at 15 °C) containing sulfur content of 922 ppmw were used in the reactions.

2.2. Sonochemical reactor system

The heating and cooling inlet to the reactor jacket are at the bottom left side of the jacket, the outlet at the top right side. A needle valve and a manometer were connected to the reactor. The temperature of the reactor was controlled by a water bath circulator and an almost constant temperature was sustained in the reactor during the reaction. The reaction was quenched with input of the tap water through the reactor jacket switching on the ball valve immediately after the desired reaction time had elapsed (Fig. 1).

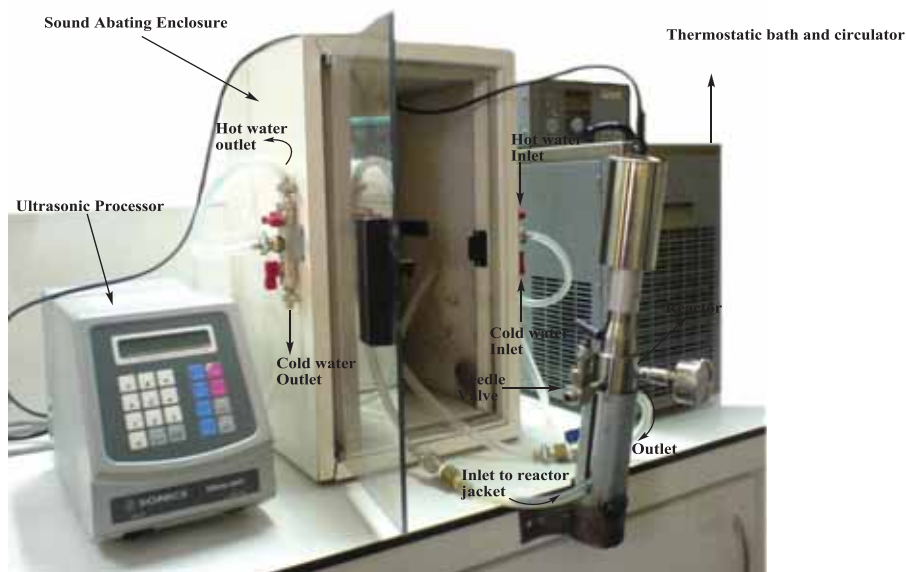


Fig. 1. Sonoreactor system

2.3. Sonocatalytic oxidations of the model sulfur compounds

Approximately 2000 ppm S solutions of T, 2-MT and 2,5-DMT were prepared by dissolving each sulfur compound in n-heptane individually. About 217 mg TBAB and thiophene solution, 35% (wt.) hydrogen peroxide solution, formic acid at S/O/F = 8/1/1 volume ratio were added into the batch stainless steel reactor. After each reaction of 15 min. at the same volume ratio and same TBAB amount at 30 and 40 °C under ultrasound irradiation in 20 kHz frequency and 50% amplitude, the aqueous phase was removed from the treated organic phase, which was then re-subjected to ODS. Oxidative reactions of 2-MT and 2,5-DMT were fulfilled at 8/1/1 volume ratios in the same way as the thiophene reactions at 30 °C. Also, one reaction of thiophene was performed at 2/1/1 volume ratio at 30 and 40 °C for 15 and 60 min. In addition, individual reaction of 2-MT, 2,5-DMT was accomplished at 8/3/3, 4/1/1 volume ratios, respectively, at 30 °C for 15 min. The volume of reaction mixtures for T, 2-MT and 2,5-DMT was in the range of 40-60 ml, depending on the volume ratios of the reactants. The equipment used was VCX (Vibra-Cell) ultrasonic processor 750 watts in power during the reactions. After the reactions, the sulfur quantity in the organic phase containing the model compounds was analyzed by Gas Chromatography (HP 6890)–Sulfur Chemiluminescence Detector (Sievers Model 355) (GC-SCD) system. A capillary column, HP19091P-S15 (HP-PLOT Al₂O₃ “S” deactivated, 50 m length 0.32 mm inner diameter 8 µm film thickness) was used for identifying all the sulfur compounds and injection volume was 1 µl.

2.4. Sonocatalytic oxidative desulfurization of diesel oil

The oxidation of diesel oil was fulfilled exactly alike the oxidations of the model sulfur compounds. ODS reactions of T922 diesel oil sample were carried out sequentially at 8/1/1 volume ratios at 30 and 40 °C for 15 min. Concerning these reactions, oxidized sulfur compounds in the organic phase were extracted only after the second and the fourth reactions, but the first and the third reactions. Furthermore, the diesel oil sample was oxidized at 2/1/1 ratios at 30 and 40 °C for 60 min. The oxidized sulfur compounds in diesel oil were extracted three times with acetonitrile. Acetonitrile to diesel oil ratio was 1/2 by weight for all the extraction operations. Total sulfur amounts in the treated diesel oil samples after reactions, followed by extraction were analyzed by ANTEK Model 9000 Sulfur analyzer for less S than 200 ppm and Oxford Model Lab-X 3500 Energy-dispersive X-ray fluorescence spectrometer for bigger S than 200 ppm in Izmit Refinery of TUPRAS.

3. Results and discussions

Fig. 2 shows that the effect of the number of stages of the reaction on thiophene conversion. While the total conversion is high in the first three stages, reaction rate diminishes towards the fourth stage.

It is interesting that the total conversion at 30 °C is higher than that at 40 °C. The reason for the increased conversion is faster decomposition of peroxyformic acid at 40 °C, which is produced in situ during the reaction of hydrogen peroxide with formic acid and necessary to oxidize the model sulfur compounds, resulting in lower conversions of T at 40 °C according to the conversions at 30 °C. While Zhao et al. [33] obtained a thiophene conversion of about 40% and 60% with S/O/F = 2/1/1 volume ratio and the same PTC at 50 °C in 15 and 30 min., respectively., we obtained a conversion of 43% with 8/1/1 volume ratio (molar ratio for H₂O₂:formic acid:sulfur of 34:78:1) at 30 °C in 15 min. Filippis et al. [35] also studied kinetic of peroxyformic acid formation in temperature range of 30-60 °C and observed peroxyformic acid formation reached a maximum and then decreased at the relevant temperatures, especially slower decomposition of peroxyformic acid at 30 °C with respect to that decompositions at 40, 50 and 60 °C and they showed that peroxyformic acid is decomposed by producing carbon dioxide and

water while hydrogen peroxide is not decomposed under the reaction conditions. In addition to this, Xiaoying et al. [36] demonstrated that the decomposition of performic acid is affected by temperature more significantly than the synthesis and hydrolysis of performic acid since activation energy of performic acid decomposition is bigger as compared to those of its synthesis and hydrolysis.

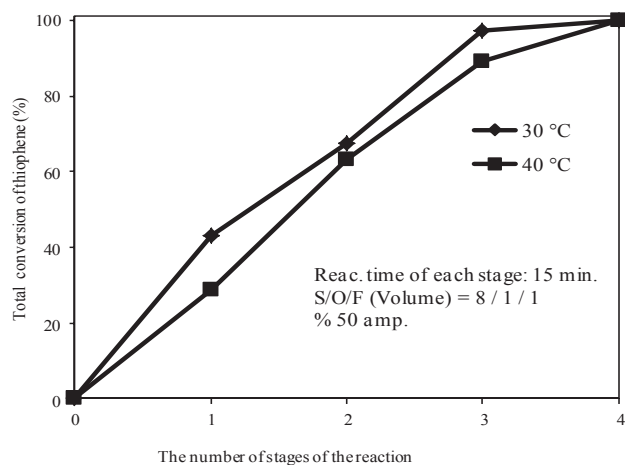


Fig. 2. The effect of reaction number on thiophene conversion

Afterwards, the reactions were performed with one addition of the reactants with 2/1/1 volume ratio for 15 and 60 min. It is seen from Fig. 3 that the conversion is 66, 73% at 30 and 40 °C, respectively, in 15 min. It can be concluded that when H_2O_2 is used in high amounts, thermal decomposition of the peroxyformic acid takes longer, readily oxidizing the thiophenes during the reaction time. Increasing the reaction time has no meaning practically since peroxyformic acid is exhausted in the first 15 min. It is seen from Fig. 3 that the sulfur removal at 60 min is about the same as that at 15 min.

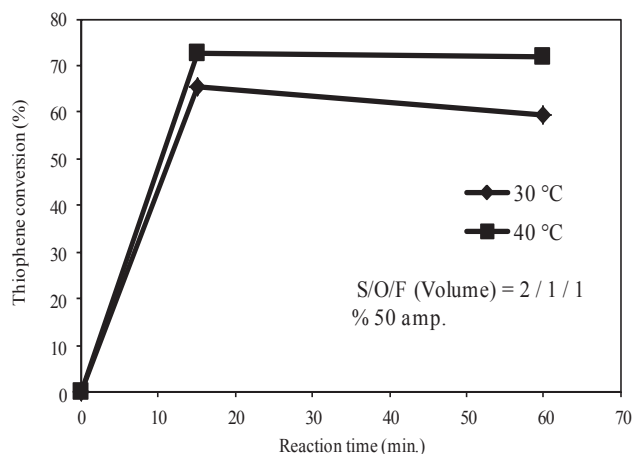


Fig. 3. Influence of reaction time on thiophene conversion

Oxidative desulfurization results of 2-MT and 2,5-DMT according to the number of the reaction at 30 °C are displayed in Fig. 4. As known, the higher the electron density on sulfur atom, the higher the oxidative desulfurization reactivity is in homogenous hydrogen peroxide-formic acid catalyst system. That's why the total removal of 2,5-DMT is easier than that of 2-MT in the reactions of 15 min. Furthermore, reaction results of the two sulfur compounds with one addition of reactants in one reaction of 15 min. at 30 °C are reported in Table 1. Though 2,5-DMT is in high volume ration, 4/1/1, in reaction mixture, its conversion is bigger than that of 2-MT because of the reason mentioned before.

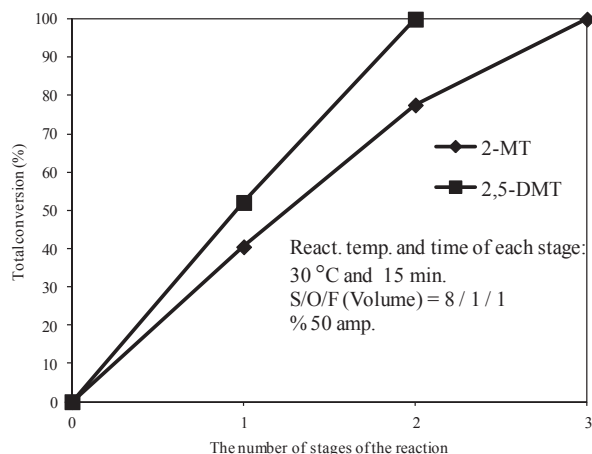


Fig. 4. Influence of reaction number on total conversion of 2-MT and 2,5-DMT

Table 1. Sulfur removal from thiophene derivatives using different reactant ratios at 30 °C

	t,min.	S ^a /O ^b /F ^c (Volume)	Conversion (%)
2-MT	15	8/3/3	74.94
2,5-DMT	15	4/1/1	71.14

Note: ^aOrganic phase containing sulfur compound, ^bhydrogen peroxide, ^c formic acid.

It is demonstrated from all of these results that to use H₂O₂ in low amounts with multiple additions of reactants instead of one addition of them is more economical and efficient. It is evident the reactions with one addition of reactants are not completed. In addition, TOAB was used to observe the effect of phase transfer catalyst on desulfurization yield for reaction of thiophene and as it is seen from Table 2, the ODS of thiophene at 30 °C is improved, compared as TBAB, 74% at 15 min. The high conversion of thiophene with TOAB is due to the fact that the alkyl chain of it is longer than that of TBAB, consequently making it more lipophilic.

Table 2. Desulfurization of thiophene using TOAB as PTC at 30 °C

t, min.	S/O/F (Vol.)	Conversion (%)
15	2/1/1	73.64

Desulfurization yields of T922 diesel oil sample under ultrasound at 30 and 40 °C are reported in Table 3. When the diesel sample is oxidized sequentially at 8/1/1 volume ratios (molar ratio for H₂O₂:formic acid:sulfur of 60:137:1) at 30 and 40 °C for 15 min., total sulfur removal is about same, around 98% wt. However, desulfurization of the diesel sample is somewhat lower at 2/1/1 volume ratios than those of the sample at 8/1/1 volume ratios at the mentioned temperatures. Sulfur compounds available in the diesel sample are more readily oxidized as compared to oxidization of T, 2-MT and 2,5-DMT. This can be due to high content of aromatic sulfur compounds such as BT, DBT etc. rather than T.

Table 3. Desulfurization of diesel fuel sample containing 922 ppm S using TBAB

t,min.	T, °C	S/O/F	Total Sulfur Removal (%)
^a 15	30	8/1/1	98.03
^b 15	30	8/1/1	98.18
60	30	2/1/1	96.19
^c 15	40	8/1/1	97.11
^d 15	40	8/1/1	98.16
60	40	2/1/1	96.71

Note: ^{a,c} Second reaction, followed by extraction, ^{b,d} fourth reaction, followed by extraction. After the first and the third reactions, sulfur compounds in the organic phase weren't extracted.

4. Conclusion

It was found that to perform sonocatalytic ODS reactions of thiophene and its derivatives sequentially at low temperatures and low formic acid-H₂O₂ amounts is more efficient because peroxyformic acid, produced in situ by H₂O₂ and formic acid, decomposes slowly at 30 °C, thus increasing the reaction conversion. It was shown that thiophene conversion is almost constant as reaction time increases from 15 min. to 60 min. Therefore, the optimum reaction time and temperature was 15 min. and 30 °C in this study. This study can be beneficial economically to increase desulfurization of diesel oils including high concentration of aromatic sulfur compounds with lower H₂O₂-HCOOH volumes in shorter times.

Acknowledgements

Thanks TUPRAS technicians to let us use ANTEK Model 9000 Sulfur Analyzer and Oxford, Model Lab-X 3500 Energy-dispersive X-ray fluorescence spectrometer for determination of total sulfur in diesel fuel samples used in our study.

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